PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-138669
(43)Date of publication of application : 31.05.1996

(51)Int.CI. H01M 4/58 H01M 4/02 H01M 10/40

(21)Application number : 06-269910 (71)Applicant : TORAY IND INC
(22)Date of filing : 02.11.1994 (72)Inventor : TAKANISHI KEIJIRO
MATSUDA YOSHIO
TSUKAMOTO JUN

(54) CATHODE ELECTROACTIVE MATERIAL, THE MANUFACTURING PROCESS, AND NON-AQUEOUS SOLVENT SECONDARY BATTERY USING THE MATERIAL

(57)Abstract:

PURPOSE: To provide a high capacity and an excellent charge - discharge cycle performance by using a compound having a specified composition with a chemical formula; $Li_{1-x}A_xNi_{1-y}B_yO_2$ as a positive active material.

CONSTITUTION:

(1) A compound having a chemical formula $Li_{1-x}A_xNi_{1-y}B_YO_2$ is used as a positive electroactive material, wherein A stands for alkali or alkaline earth metal elements, B for at least one sort of transition metal elements, $0<x<=0.10$, $0<y<=0.30$ mole ratio. When B consists of two or more kinds of transition metal elements, y means the total mole ratio of the transition metal elements. And when y=0, A contains at least an alkaline earth metal.

(2) A starting raw material containing lithium or A is added to a starting raw material containing nickel or B in the stoichiometric ratio (of the former to the latter) from 1.05 to 1.25, the raw materials are fired in oxygen atmosphere, and non-reacted alkali components are removed. As a result, the amount of an alkali metal with which lithium is substituted can be lessened and thus the decrease of the initial capacity is suppressed.

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CLAIMS

[Claim(s)]

[Claim 1] The electroactive material using a compound expressed with chemical formula; $Li_{1-x}A_xNi_{1-y}B_yO_2$, wherein A is alkali or alkaline-earth metal element, and B is at least one sort of transition-metal elements. $0<x<=0.10$, $0<y<=0.30$. When B consists of two or more kinds of transition metal elements, y means the total mole ratio of the transition metal elements. And when y=0, A contains at least an alkaline earth metal.

[Claim 2] The manufacturing method of the positive electroactive material according to Claim 1, wherein a starting raw material containing lithium or A is added to a starting raw material containing nickel or B in the stoichiometric ratio of 1.05 to 1.25 to the latter, and the non-reacted alkaline components are removed after the raw materials are fired in oxygen atmosphere.

[Claim 3] The manufacturing method of the positive electroactive material according to Claim 2, wherein the removal of the said alkaline components is carried out by washing with water.

[Claim 4] The non-aqueous-solvent rechargeable battery characterized by using a positive electroactive material according to Claim 1.

[Claim 5] The non-aqueous-solvent rechargeable battery according to Claim 4 characterized by using the positive electroactive material manufactured by the method according to Claim 2.

[Claim 6] The non-aqueous-solvent rechargeable battery according to Claim 4 or 5 characterized by using a carbonaceous material for a negative electroactive material.

[Claim 7] The non-aqueous solvent rechargeable battery given in any one claim out of the Claims 4-6 to which this carbonaceous material is characterized by carbon fiber.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0012] [Purpose of this invention]

To offer a cathode active material which has high capacity and good cycleability, and secondary battery using this cathode material.

[0028]

[Example]

[Table 1]

表1.　実施例の仕込み組成と定量分析組成

	上段：仕込み組成／下段：定量分析組成
実施例1	$Li_{1.29}Ba_{0.025}Ni_{1.00}O_2$ $Li_{0.98}Ba_{0.021}Ni_{1.0}O_2$
実施例2.	$Li_{1.29}Sr_{0.025}Ni_{1.00}O_2$ $Li_{0.98}Sr_{0.021}Ni_{1.0}O_2$
実施例3.	$Li_{1.07}K_{0.039}Ni_{0.900}Mn_{0.100}O_2$ $Li_{0.97}K_{0.030}Ni_{0.90}Mn_{0.10}O_2$
実施例4.	$Li_{1.07}Na_{0.036}Ni_{0.90}Mn_{0.100}O_2$ $Li_{0.97}Na_{0.031}Ni_{0.90}Mn_{0.10}O_2$
実施例5.	$Li_{1.08}Ba_{0.022}Ni_{0.900}Mn_{0.100}O_2$ $Li_{0.98}Ba_{0.020}Ni_{0.90}Mn_{0.10}O_2$
実施例6.	$Li_{1.05}Ba_{0.055}Ni_{0.900}Mn_{0.100}O_2$ $Li_{0.95}Ba_{0.051}Ni_{0.90}Mn_{0.10}O_2$
実施例7.	$Li_{0.990}Ba_{0.11}Ni_{0.900}Mn_{0.100}O_2$ $Li_{0.90}Ba_{0.10}Ni_{0.90}Mn_{0.10}O_2$
実施例8.	$Li_{1.18}Ba_{0.024}Ni_{0.800}Mn_{0.200}O_2$ $Li_{0.98}Ba_{0.021}Ni_{0.80}Mn_{0.20}O_2$
実施例9.	$Li_{1.18}Ba_{0.024}Ni_{0.700}Mn_{0.300}O_2$ $Li_{0.98}Ba_{0.021}Ni_{0.70}Mn_{0.30}O_2$
実施例10.	$Li_{1.03}Ba_{0.021}Ni_{0.900}Co_{0.100}O_2$ $Li_{0.98}Ba_{0.020}Ni_{0.90}Co_{0.10}O_2$
実施例11.	$Li_{1.03}Ba_{0.021}Ni_{0.900}Ti_{0.100}O_2$ $Li_{0.98}Ba_{0.019}Ni_{0.90}Ti_{0.10}O_2$
実施例12.	$Li_{1.03}Ba_{0.021}Ni_{0.900}Cu_{0.100}O_2$ $Li_{0.98}Ba_{0.020}Ni_{0.90}Cu_{0.10}O_2$
実施例13.	$Li_{1.08}Mg_{0.022}Ni_{0.900}Co_{0.100}O_2$ $Li_{0.98}Mg_{0.021}Ni_{0.90}Co_{0.10}O_2$
実施例14.	$Li_{1.08}Sr_{0.022}Ni_{0.900}Co_{0.100}O_2$ $Li_{0.98}Sr_{0.020}Ni_{0.90}Co_{0.10}O_2$
実施例15.	$Li_{1.10}Ni_{0.900}Mn_{0.050}Co_{0.050}O_2$ $Li_{1.0}Ni_{0.90}Mn_{0.051}Co_{0.049}O_2$
実施例16.	$Li_{1.10}Ni_{0.800}Mn_{0.100}Co_{0.100}O_2$ $Li_{1.0}Ni_{0.80}Mn_{0.10}Co_{0.10}O_2$
実施例17.	$Li_{1.10}Ni_{0.700}Mn_{0.100}Co_{0.200}O_2$ $Li_{1.0}Ni_{0.70}Mn_{0.10}Co_{0.20}O_2$
実施例18.	$Li_{1.10}Ni_{0.800}Mn_{0.100}Cu_{0.100}O_2$ $Li_{1.0}Ni_{0.80}Mn_{0.10}Cu_{0.10}O_2$

Upper : Synthesis ratio

Lower : Measured by ICP

[Table 2]

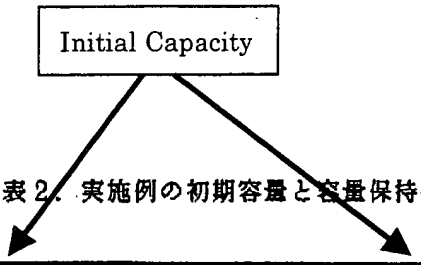
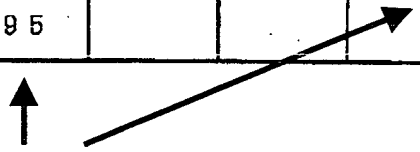


表2. 実施例の初期容量と容量保持率

	初期容量 (mAh/g)	容量保持率 (%)		初期容量 (mAh/g)	容量保持率 (%)
実施例1	135	88	実施例11	144	94
実施例2	138	90	実施例12	142	92
実施例3	135	85	実施例13	140	92
実施例4	135	82	実施例14	148	95
実施例5	140	94	実施例15	138	90
実施例6	138	87	実施例16	138	88
実施例7	130	85	実施例17	135	86
実施例8	138	93	実施例18	135	92
実施例9	135	85	実施例19	140	94
実施例10	144	95			



Efficiency = Capacity @ 100th cycle / Capacity @ 1st cycle *100

[0036]

The Example of comparison

[Table 4]

表４．比較例の仕込み組成と定量分析組成

	上段：仕込み組成／下段：定量分析組成
比較例１	$Li_{1.08}Ni_{1.00}O_2$ $Li_{1.0}Ni_{1.0}O_2$
比較例２．	$Li_{0.880}Ba_{0.220}Ni_{0.900}Mn_{0.100}O_2$ $Li_{0.80}Ba_{0.20}Ni_{0.90}Mn_{0.10}O_2$
比較例３．	$Li_{1.08}Ba_{0.022}Ni_{0.600}Mn_{0.400}O_2$ $Li_{0.98}Ba_{0.020}Ni_{0.60}Mn_{0.40}O_2$
比較例４．	$Li_{1.10}Ni_{0.600}Mn_{0.100}Co_{0.100}O_2$ $Li_{1.0}Ni_{0.60}Mn_{0.10}Co_{0.10}O_2$
比較例５．	$Li_{0.980}Ba_{0.020}Ni_{0.800}Mn_{0.200}O_2$ $Li_{0.83}Ba_{0.017}Ni_{0.80}Mn_{0.20}O_2$
比較例６．	$Li_{1.18}Ba_{0.024}Ni_{0.800}Mn_{0.200}O_2$ $Li_{1.13}Ba_{0.023}Ni_{0.80}Mn_{0.20}O_2$

Washed to remove excessive alkalinity

[Table 3]

表３．比較例の初期容量と容量保持率

	初期容量 (mAh/g)	容量保持率 (%)
比較例１	１３０	４５
比較例２	１１０	７５
比較例３	１３０	５０
比較例４	１３０	５８
比較例５	１００	２０
比較例６	評価不能	評価不能
比較例７	１２８	４１